Laboratory of Surface Chemistry (Special Issue on the Commemoration of the Fiftieth Anniversary)

Bull. Inst. Chem. Res., Kyoto Univ., Vol. 54, No. 6, 1976

LABORATORY OF SURFACE CHEMISTRY

Head: Dr. Tohru Takenaka

Gotoh laboratory was established in 1947 for physico-chemical studies of surface and colloid chemistry and officially named "Laboratory of Colloid Chemistry" in 1964. After the retirement of Professor Rempei Gotoh in 1969, Professor Tohru Takenaka succeeded him as the head of the laboratory in 1971. The official name of the laboratory was changed to "Laboratory of Surface Chemistry" in 1975.

Scientific works carried out in this laboratory before 1966 were reviewed in the Special Issue on the Commemoration of the Fortieth Anniversary of the Institute for Chemical Research. Since that time, vibrational spectra of surface thin films and of surface-chemically interesting materials and electrical phenomena at interfaces were studied in collaboration with Assistant Professor Dr. Soichi Hayashi, Dr. Mutsuo Matsumoto, Mr. Junzo Umemura, and Mr. Noriyuki Kimura. A brief description of the works published during these ten years will be given below.

I. Vibrational Spectra of Surface Thin Films

1. Resonance Raman Spectra of Adsorbed Monolayers

Studies of molecular orientation in monolayers adsorbed at the liquid-gas and liquid-liquid interfaces are a subject of much interest in the field of surface chemistry. We have studied the resonance Raman spectra of monolayers of complexes of cationic surfactants and anionic azo dyes adsorbed at the interface between carbon tetrachloride and aqueous solutions using the total reflection method of the exciting light (laser beam) at the interface. From polarization measurements of the Raman spectra, the orientation of the dye molecules in the monolayers was discussed. The same type of studies were also carried out for monolayers of surface-active azo dyes adsorbed at the oil-water and air-water interfaces. It was found that there was good correspondence between the states of monolayers and the molecular orientations and that the planes of the chromophore of the dye molecules had a tendency to subtend an angle with the interface with increasing the amount of the adsorbed molecules.

2. Infrared Spectra of Surface Thin Films

Thin films adsorbed at the gas-solid and liquid-solid interfaces were studied by using the infrared transmission and attenuated total reflection (ATR) methods. Built-up films of long-chain fatty acids transferred from monolayers spread on substrates onto germanium plates were also studied by the ATR method. The use of polarized infrared radiation allowed us discussions about molecular structure and orientation in surface films. It was concluded that the built-up and adsorbed films of the long-chain fatty acids consisted of an assembly of monoclinic crystallites which were uniaxially oriented with respect to the normal axis to the interface.

II. Molecular Orientation

1. Simultaneous Measurements of Stress and Infrared Dichroism of Polymer Films

The method for simultaneous measurements of stress and infrared dichroism of polymer films was devised by using a double beam infrared spectrophotometer. The time dependence of the infrared dichroism was obtained by measuring the intensity change at peak maxima on the differential polarized infrared spectra. The method was applied to studies of continuous elongation and stress relaxation of various polymers such as natural rubber, polyethylene, polychloroprene, and polyvinylchloride containing diethyl phthalate or dioctyl phthalate as plasticizer.

2. Precise Measurements of Dichraic Ratio by Spectropolarimeter

Precise measurements of dichroic ratio close to unity were made with a spectropolarimeter. By this method, slight orientation of small molecules induced by the following methods was investigated; (a) irradiation of polarized monochromatic light to various dyes dispersed in polymer films, (b) stretching of polyvinylchloride films containing the anthracene molecules, and (c) application of high electric field to small molecules having large dipole moments, *p*-nitroaniline and N,N-dimethyl-*p*-nitroaniline, in various solvents.

III. Vibrational Spectra of Molecular Crystals

1. Molecular Structure of Crystalline Fatty Acids

Infrared and Raman spectra of normal fatty acids were studied in the range from room to liquid-helium temperatures. Great temperature dependences were observed at characteristic frequencies of the carboxyl group and in the region of the band progression due to the CH_2 wagging modes. These results suggest that the two distinct configurations, *cis* and *trans* forms for the C_β–C_α–C=0 group, coexist in the crystalline state. Enthalpy and entropy differences between the two forms were obtained from the temperature dependence of band intensities.

2. Vibrational Spectra of Fully Conjugated Tetracyano-Compounds

Fully conjugated tetracyano-compounds such as tetracyanoethylene, 7,7,8,8–tetracyanoquinodimethane and 1,2,4,5-tetracyanobenzene are known to be strong electron acceptors in charge-transfer complexes. Infrared and Raman spectra of these compounds and their deuterated derivatives were examined. From polarization measurements of the infrared and Raman spectra of the crystals, the bands were experimentally classified into respective symmetry species under the assumption of the oriented gas model. The assignments of the observed frequencies to the fundamental modes were carried out with the aid of comparison of the spectral data with those of analogous molecules, application of the product rule and the normal coordinate analysis. The same examinations were also made for thiocyano-compounds such as tetracyano-1,4-dithiin and tetracyanothiophene.

IV. Electrical Phenomena at Interfaces

1. Electrocapillarity at Liquid-Liquid Interfaces

a) The coalescence of liquid droplets in aqueous and non-aqueous solutions in the presence and absence of surfactant was investigated by applying the polarizing potential. The experimental results were explained in the same mechanism as the stability of disperse systems. b) In order to study the double layer structure at oil-water interfaces the electrocapillary curve was measured at different concentrations of various kinds of electrolytes.

2. Double Layer Interactions in Thin Liquid Films

The drainage process of thin liquid films between two phases was measured as a function of time by using the capacitance and optical reflection methods. The disjoining pressure which was experimentally determined from the drainage rate is analysed in terms of electrostatic force and attraction, the characteristic of attraction constant between two phases as well as the mechanism of coagulation of disperse systems being investigated.

Publications

(* indicates an article published in Japanese)

I. Vibrational Spectra of Surface Thin Films

1. S. Hayashi, T. Takenaka, and R. Gotoh: Infrared Spectra of Acetic Acid Adsorbed on Alumina in Carbon Tetrachloride, *J. Chem. Soc. Japan, Pure Chem. Sec.*, **88,** 133 (1967).*
2. T. Takenaka, S. Tadokoro, and N. Uyeda: Infrared Absorption Spectra of Tetracyanoethylene Adsorbed on Evaporated Alkali Halides, *Bull. Inst. Chem. Res., Kyoto Univ.*, **48,** 249 (1970).
3. T. Takenaka, K. Nogami, H. Gotoh, and R. Gotoh: Studies of Built-Up Films by Means of the Polarized Infrared ATR Spectrum (I) Built-Up Films of Stearic Acid, *J. Colloid Interface Sci.*, **35,** 395 (1971).
4. T. Takenaka, K. Nogami, and H. Gotoh: Studies of Built-Up Films by Means of the Polarized Infrared ATR Spectrum (II) Mixed Films of Stearic Acid and Barium Stearate, *ibid.*, **40,** 409 (1972).
5. T. Takenaka and K. Nogami: Studies of Built-Up Films by Means of the Polarized Infrared ATR Spectrum (III) Elaidic Acid Films, *Bull. Chem. Soc. Japan,* **45,** 2367 (1972).
6. K. Wada, T. Takenaka, S. Hayashi, and S. Takeno: Infrared Spectral Studies of Hydrogen Fluoride Adsorbed on Potassium Bromide, *Japan J. Appl. Phys., Suppl.* **2,** Pt. 2. 109 (1974).
7. T. Higashiyama and T. Takenaka: Infrared Attenuated Total Reflection Spectra of Adsorbed Layers at the Interface between a Germanium Electrode and an Aqueous Solution of Sodium Laurate, *J. Phys. Chem.*, **78,** 941 (1974).
8. T. Takenaka, K. Harada, and T. Nakanaga: Raman Spectra of Benzene, Ethyl Benzene and Dimethyl Phthalate Solubilized in Aqueous Solution of Surface-Active Agents, *Bull. Inst. Chem. Res., Kyoto Univ.*, **53,** 173 (1975).
9. T. Takenaka and T. Nakanaga: Resonance Raman Spectra of Monolayers Adsorbed at the Interface between Carbon Tetrachloride and an Aqueous Solution of a Surfactant and a Dye, *J. Phys. Chem.*, **80,** 475 (1976).
10. T. Nakanaga and T. Takenaka: Resonance Raman Spectra of Monolayers of a Surface-Active Dye Adsorbed at the Oil-Water Interface, *ibid.*, **81,** (1977), in press.

Reviews

11. T. Takenaka: Studies of Adsorbed Molecules by Means of Infrared Spectra, *Hyomen (Surface)*, **4**, 301, 373 (1966).*
12. T. Takenaka: Studies of Monomolecular Layers by Means of Infrared Spectra, *ibid.*, **8**, 636 (1970).*
13. T. Takenaka: Studies of Surface Chemistry by Means of Raman Spectra, *ibid.*, **14**, 303 (1976).*
14. T. Takenaka: Molecular Orientation in Surface Thin Films, *Maku (Membrane)*, **2**, 25 (1977).*

Books

15. N. Sheppard, N. R. Avery, M. Clark, B. A. Morrow, R. St. C. Smart, T. Takenaka, and J. W. Ward: "Molecular Spectroscopy", Ed. P. Heppel, Recent Advances in the Infrared Spectroscopy of Adsorbed Molecules. The Institute of Petroleum, London (1968), P. 97.
16. T. Takenaka: "Laser Raman Spectroscopy and Its Applications", Ed. T. Shimanouchi, M. Tasumi, and I. Harada, Chap. 7, Resonance Raman Scattering, Sec. V, Studies of Monomolecular Layers Adsorbed at the Oil-Water Interface. Nankodo, Tokyo (1977), in press.*

II. Molecular Orientation

1. R. Gotoh, T. Takenaka, and N. Hayama: Simultaneous Measurements of Stress Relaxation and Infrared Dichroic Change of Polymers, *Reports Progress Polymer Phys. Japan*, **9**, 453 (1966).
2. R. Gotoh, T. Takenaka, J. Umemura, and S. Hayashi: Simultaneous Measurements of Stress and Infrared Dichoism of Inflated Polyethylene Films, *Bull. Inst. Chem. Res., Kyoto Univ.*, **44**, 286 (1966).
3. R. Gotoh, T. Takenaka, and N. Hayama: Simultaneous Measurements of Stress and Infrared Dichroism on Polymers (I) Stress Relaxation of Vulcanized Natural Rubber, *Rubber Chem. Tech.*, **40**, 663 (1967).
4. T. Takenaka, Y. Shimura, and R. Gotoh: Simultaneous Measurements of Stress and Infrared Dichroism of Polychloroprene, *Bull. Inst. Chem. Res., Kyoto Univ.*, **46**, 220 (1968).
5. J. Umemura, T. Takenaka, S. Hayashi, and R. Gotoh: Infrared Dichroism and Orientation of Plasticizers in Stretched Polyvinylchloride Films, *ibid.*, **46**, 228 (1968).
6. R. Gotoh, N. Kimura, and S. Hayashi: Sensitive Measurements of Photodichroism of Dyes by Spectropolarimeter, *ibid.*, **47**, 340 (1969).
7. R. Gotoh, N. Kimura, and S. Hayashi: Optical Rotatory Dispersion Induced by Molecular Orientation, *ibid.*, **47**, 349 (1969).
8. T. Takenaka, Y. Shimura, and R. Gotoh: Simultaneous Measurements of Stress and Infrared Dichroism on Polymers (II) Continuous Elongation and Stress Relaxation of Polychloroprene, *Kolloid Z. u. Z. Polymere*, **237**, 193 (1970).
9. R. Gotoh, N. Kimura, and S. Hayashi: Studies on Molecular Orientation by Spectropolarimeter, *J. Chem. Soc. Japan*, **73**, 1483 (1970).*
10. J. Furukawa, E. Kobayashi, K. Uratani, Y. Iseda, J. Umemura, and T. Takenaka: Infrared Absorption Spectra of Alternating Copolymers of Butadiene with Acrylonitrile and Deuterated Analogues, *Polymer J.*, **4**, 358 (1973).
11. N. Kimura and S. Hayashi: Orientation of Anthracene in Stretched Polyvinylchloride, *Bull. Inst. Chem. Res., Kyoto Univ.*, **54**, 263 (1976).

Reviews

12. T. Takenaka: Differential Polarized Infrared Spectrum and Its Applications. *The Hitachi Sci. Inst. News*, **9**, 375 (1966).*
13. S. Hayashi: Measurements of Infrared Dichroism, *Jasco Report*. **3**, No. 7, 11 (1966).*
14. R. Gotoh: Studies of Orientation of Polymers by Differential Polarized Infrared Spectra, *Nippon Gom Kyokai Shi*, **41**, 1035 (1968).*
15. S. Hayashi and N. Kimura: Precise Measurements of Dichroism by ORD, *Jasco Report*, **11**, No. 9, 1 (1974).*

III. Vibrational Spectra of Molecular Crystals

1. S. Hayashi and N. Kimura: Infrared Spectra and Molecular Configuration of Benzoic Acid, *Bull. Inst. Chem. Res., Kyoto Univ.*, **44**, 335 (1966).
2. S. Hayashi, H. Hara, and N. Kimura: Infrared Spectra and Molecular Configuration of Dimeric Carboxylic Acids, *ibid.*, **46**, 213 (1968).
3. T. Takenaka: Infrared and Raman Spectra of TCNQ and TCNQ-d_4 Crystals, *ibid.*, **47**, 387 (1969).
4. T. Takenaka: Molecular Vibrational Spectra of Tetracyanoquinodimethane and Tetracyanoquinodimethane-d_4 Crystals, *Spectrochim. Acta*, **27A**, 1735 (1971).
5. S. Hayashi and J. Umemura: Coexistence of Two Molecular Configurations in Crystalline Carboxylic Acid, *Acta Cryst.*, **A28**, s239 (1972).
6. J. Umemura and T. Takenaka: Cartesian Displacements of Normal Vibrations of 1,2,4,5-Tetracyanobenzene and 1,2,4,5-Tetracyanobenzene-d_2 Molecules, *Bull. Inst. Chem. Res., Kyoto Univ.*, **51**, 206 (1973).
7. S. Hayashi and J. Umemura: Disappearances of COOH Infrared Bands of Benzoic Acid, *J. Chem. Phys.*, **60**, 2630 (1974).
8. K. Machida, Y. Kuroda, T. Uno, and S. Hayashi: Lattice Vibrations and Raman Band Splittings of Dipropionamide, *Spectrochim. Acta*, **30A**, 125 (1974).
9. J. Umemura and S. Hayashi: Infrared Spectra and Molecular Configurations of Liquid and Crystalline Acrylic Acids, *Bull. Inst. Chem. Res., Kyoto Univ.*, **52**, 585 (1974).
10. J. Umemura and S. Hayashi: Intermolecular Force and Stable Configuration of Crystalline Benzoic Acid, *ibid.*, **53**, 180 (1975).
11. S. Hayashi and J. Umemura: Infrared Spectroscopic Evidence for the Coexistence of Two Molecular Configurations in Crystalline Fatty Acids, *J. Chem. Phys.*, **63**, 1732 (1975).
12. T. Takenaka, J. Umemura, S. Tadokoro, S. Oka, and T. Kobayashi: Vibrational Spectra of 1,2,4,5-Tetracyanobenzene and 1,2,4,5-Tetracyanobenzene-d_2 Crystals, *Spectrochim. Acta*, **33A**, (1977), in press.
13. J. Nakanishi and T. Takenaka: Vibrational Spectra of Tetracyanothiophene, *Bull. Chem. Soc. Japan*, **50**, 36 (1977).
14. Y. Kato, T. Kurimoto, and T. Takenaka: Polarized Raman Spectra of Lanthanium Ethylsulfate Nonahydrate and Potassium Ethysulfate Crystals. *Spectrochim. Acta*, **33A**, (1977), in press.
15. J. Nakanishi and T. Takenaka: Vibrational Spectra of Tetracyano-1,4-dithiin, *Bull. Chem. Soc. Japan*, submitted for publication.

Reviews

16. S. Hayashi, N. Kimura, and J. Umemura: Sampling Method in Infrared Spectroscopy, *Bunseki Kiki*, **3**, No. 12, 9 (1965); **4**, No. 2, 46 (1966); **4**, No. 3, 58 (1966); **4**, No. 7, 38 (1966).*
17. T. Takenaka and J. Umemura: Infrared and Raman Spectra, *Japan Analyst. Annual Review*, **17**, 22R (1968).*
18. T. Takenaka, S. Hayashi, and J. Umemura: Infrared and Raman Analyses, *ibid.*, **19**, 41R (1970).*

Book

19. K. Machida, T. Takenaka, and T. Uno: "The Instrumental Method for Analytical Chemistry". Japan Soc. Anal. Chem., 5th Ed. Chap. 7, Analyses by Infrared Absorption Spectra, Kagaku-Dojin, Tokyo (1969).*

IV. Electrical Phenomena at Interfaces

1. A Watanabe, M. Matsumoto, and R. Gotoh: The electrocapillarity of Oil-Water Interfaces, *Bull. Inst. Chem. Res., Kyoto Univ.*, **44**, 273 (1966).
2. A. Watanabe, M. Matsumoto, H. Tamai, and R. Gotoh: Electrocapillary Phenomena at Oil–Water Interfaces. 1. Electrocapillary Curves at Oil-Water Interfaces, *Kolloid-Z.*, **220**, 152 (1967).
3. A. Watanabe, M. Matsumoto, H. Tamai, and R. Gotoh: Electrocapillary Phenomena at Oil-Water Interface. 2. The Counter-Ion Binding at Oil-Water Interfaces, *ibid.*, 47 (1967).

4. A. Watanabe, M. Matsumoto, H. Tamai, and R. Gotoh: Electrocapillary Phenomena at Oil–Water Interfaces. 3. The Behavior of Lecithin at Oil-Water Interfaces, *Kolloid-Z.*, **228**, 58 (1968).
5. A. Watanabe, H. Tamai, M. Matsumoto, and R. Gotoh: The Interaction between the Surface Active Agents and Dye Staffs at Oil-Water Interfaces, *J. Chem. Soc. Japan*, **90**, 738 (1969).*
6. M. Matsumoto: Studies on the Coalescence of Liquid Droplets. 1. The Influence of the Polarizing Potential on the Coalescence of Mercury Droplets in Oil Solution, *Bull. Inst. Chem. Res., Kyoto Univ.*, **47**, 354 (1969).
7. M. Matsumoto: Studies on the Coalescence of Liquid Droplets. 2. The Influence of the Polarizing Potential on the Coalescence of Aqueous Droplets in Oil Solutions, *ibid.*, **47**, 361 (1969).
8. M. Matsumoto: Studies on the Coalescence of Liquid Droplets. 3. The Influence of the Polarizing Potential on the Coalescence of Oil Phases in Aqueous Solutions, *ibid.*, **47**, 371 (1969).
9. M. Matsumoto: Studies on the Coalescence of Liquid Droplets. 4. The Coalescence of Mercury Droplets in Mixed Solvents, *ibid.*, **48**, 171 (1970).
10. M. Matsumoto: The Coagulation and Coagulating Agent for Lyophobic Colloids, *Mol.*, **11**, 85 (1973).*
11. M. Matsumoto, Y. Sakamori, K. Nishizawa, and A. Watanabe: The Adsorption of Ethylene Glycols and Their Cyclic Compounds at the Mercury-Aqueous Solution Interface, *Colloid and Polymer Science*, **252**, 478 (1974).
12. H. E. Ries, Jr., M. Matsumoto, N. Uyeda, and E. Suito: Electron Micrographs of Lecithin Films, *Bull. Inst. Chem. Res., Kyoto Univ.*, **53**, 77 (1975).
13. H. E. Ries, Jr., M. Matsumoto, N. Uyeda, and E. Suito: Electron Microscope Studies of Monolayers of Lecithin, *Adv. Chem. Series*, **144**, 286 (1975).
14. M. Matsumoto, C. Montandon, and S. Hartland: The Interaction Force in a Monomolecular Film at Low Surface Pressure, *Colloid and Polymer Sci.*, in press.
15. H. E. Ries, Jr., M. Matsumoto, N. Uyeda, and E. Suito: Electronmicroscope Studies of Monolayers of Cholesterol, *International Congress Surface Active Substances*, **7**, (1976), in press.

Review

16. M. Matsumoto: The Coalescence Mechanism of Liquid Droplets and Stability of Disperse System, *Hyomen (Surface)*, **9**, 266 (1971).*

V. Colloid and Rheology

1. R. Gotoh and K. Shimizu: Correlation between Shear Modulus and Shear Strength of Bentonite Gels, *J. Soc. Materials Sci. Japan*, **15**, 283 (1966).*
2. K. Shimizu and R. Gotoh: Viscoelastic Properties and Slip Fracture of Bentonite Gels. I, *J. Soc. Materials Sci. Japan*, **16**, 453 (1967).*
3. K. Shimizu and R. Gotoh: Viscoelastic Properties and Slip Fracture of Bentonite Gel. II, *J. Soc, Materials Sci. Japan*, **17**, 279 (1968).*

Books

4. R. Gotoh and A. Watanabe (Translation): "Colloid Chemistry" by M. J. Vold and K. Z. Vold, Kyoritsu Pub. Co. Tokyo (1966).*
5. R. Gotoh and K. Aoki (Edition): "Physical Chemistry", Hirokawa, Tokyo (1967).*

VI. Miscellaneous

1. T. Takenaka and R. Gotoh: Studies of Ion-Exchange Reaction of Metal Salts of Fatty Acids in Alkali Halide Pellets by Mean of Infrared Absorption Spectra, *Bull. Inst. Chem. Res., Kyoto Univ.*, **50**, 577 (1972).
2. T. Fujinaga, T. Takenaka, and T. Muroga: The Origin of the Archaeological Amber in Japan—Studies by Infrared Spectra, *J. Chem. Soc. Japan*, **1974** 1653.*
3. T. Fujinaga, T. Takenaka, and T. Muroga: The Origin of the Foreign and Japanese Ambers Studied by the Elemental Analyses and the Infrared Spectroscopy, *Japan Analyst*, **25**, 795 (1976).*

4. S. Ohata, T. Shidei, T. Muroga, and T. Takenaka: A Method on the Classification of Genus Pinus —Infrared Spectroscopic Analysis on the Rosin of Pinus, *J. Japanese Forestry Soc.* (1977), in press.*

Review

5. T. Takenaka: Electronegativity, *Kagaku* (*Chemistry*), **24**, 394 (1966).*

Book

6. R. Gotoh: "Physical Constants", Ed. by Kagaku Kogyo Kai, Vol. 6, Physical Constants for Combution, Maruzen, Tokyo (1968).*